

Synthesis and Thermoelectric Properties of $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ and $\text{CoAs}_{(3-x)}\text{P}_x$ Skutterudites

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Abstract

Two types of promising phosphide skutterudite materials, $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ ($x = 0.025$ to 0.70) and $\text{CoAs}_{(3-x)}\text{P}_x$ ($x = 0.5$ to 0.10), have been synthesized and their transport properties measured. These compounds were prepared using a direct synthesis technique. The samples were hot pressed and analyzed by electron microprobe microscopy. Hall Effect measurements were conducted to determine the electrical conductivity, mobility and carrier concentration. In addition, Seebeck voltage and thermal conductivity measurements were performed. The thermoelectric properties are presented and discussed as a function of temperature up to 1273 K . The thermal stability of the primary CoP_3 was examined in a static vacuum under isothermal and in-gradient conditions. The effect of the presence of 1 atm of a cover gas on the material loss rate was analyzed.

INTRODUCTION

The Jet Propulsion Laboratory (JPL) has been developing Skutterudite compounds for use in high efficiency thermoelectric devices [1-4]. One compound, CoAs_3 , has been successfully and repeatedly synthesized. Addition of P in the matrix is expected to increase the decomposition temperature and potentially enhance performance at temperatures greater than 900 K . In addition, theoretical calculations made at JPL have indicated that solid solutions of skutterudites could reduce the lattice thermal conductivity [5]. Present synthesis efforts have produced $\text{CoAs}_{(3-x)}\text{P}_x$ with x up to 0.3 (10%). Previous work has also demonstrated that large amounts of CoP_3 can be prepared using direct reaction of stoichiometric amounts of pure elemental mixtures and establishing a repeatable synthesis process [6]. The added contribution of Ni in the lattice resulting from solid solutions of CoP_3 with NiP_3 is expected to provide additional conduction electrons producing n-type conductivity. Efforts have focused on achieving up to 70% Ni incorporation. Present efforts have produced $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ with x up to 0.07 (7%) with indications that at least 30% is possible. This work discusses the process used to produce solid solutions CoP_3 and NiP_3 along with that of CoAs_3 and CoP_3 along with initial thermoelectrical property measurements and thermal stability characteristics measurements for the primary CoP_3 matrix.

Experimental Details

Stoichiometric amounts of cobalt and phosphorus and Ni were reacted using a direct synthesis technique at temperatures ranging from 873 to 1223 K . High purity cobalt (99.995% at -22 mesh), phosphorus (99.999% at -200 mesh) and Ni (99.9% at -100 mesh) were premixed for 5 minutes in a polystyrene container with an agate ball using a high-speed shaker. A uniform mixture of small grain size was used to

allow the cobalt and nickel to take up the free phosphorus at a low enough temperature during the reaction to prevent the buildup of excessive pressures within the ampoule resulting in an explosion. A 1.5 g mixture was then sealed under vacuum ($< 1 \times 10^{-5}$ torr) in thick wall (1.5 mm) quartz ampoules. The ampoules were inserted into a furnace under nearly isothermal conditions ($< 0.25\text{ K/cm}$). The samples were reacted over several temperature steps from a 473 K stabilization to a final soak at 1223 K . Rapid cooling at the end of the process is achieved by stopping the furnace and allowing the samples to cool naturally.

A similar process was used to prepare the $\text{CoAs}_{(3-x)}\text{P}_x$ compounds. The synthesis process for these materials however consisted of a 25 K/hr ramp to a 923 K soak. The synthesized samples were ground to < 150 mesh and hot pressed prior to characterization. The hot pressed samples were in the form of pellets 1.2 cm in diameter and about 1.2 cm long. The samples were then subjected to electron microprobe analysis to determine their composition. Microprobe images of two $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ sample are shown in Figure 1. The majority of the matrix in both samples is single phase. Some the unincorporated combined Ni and P

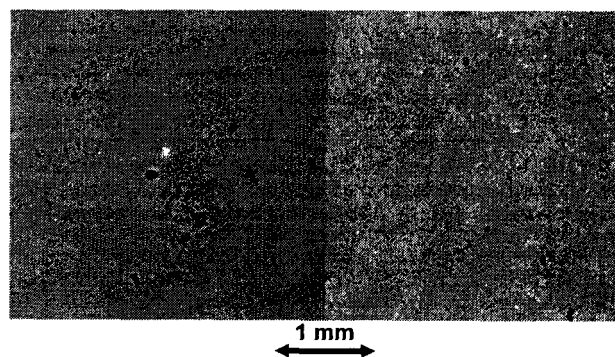


Figure 1. Electron micrographs of $\text{Co}_{0.95}\text{Ni}_{0.05}\text{P}_3$ and $\text{Co}_{0.93}\text{Ni}_{0.07}\text{P}_3$ respectively (left to right). Dark areas are pores while the white regions are various nickel phosphide compounds

compounds are observed as the localized white regions in each micrograph. The maximum amount of Ni in the analyzed samples was 7% although some of the unanalyzed samples may have up to 30% Ni.

Micrographs of $\text{CoAs}_{(3-x)}\text{P}_x$ compounds are shown in Figure 2. The maximum amount of P incorporated so far was 10%. As noted in Figure 1, the dark regions are pores while the white regions are as rich. The dark regions are larger in

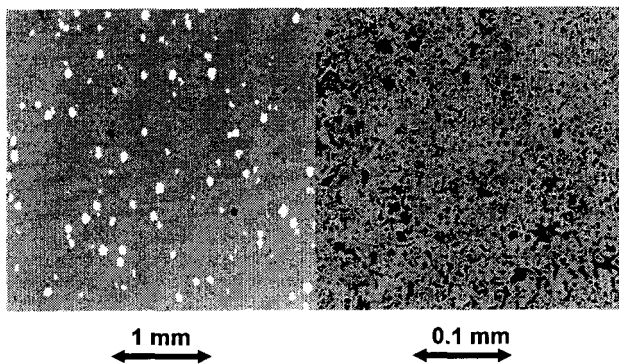


Figure 2. Electron micrographs of $\text{CoAs}_{2.83}\text{P}_{0.17}$ and $\text{CoAs}_{2.70}\text{P}_{0.30}$ respectively (left to right). Dark areas are pores while the white regions are As rich regions.

the rightmost sample due to a 10 times magnification. Most of the samples are single phase (i.e. grey areas).

Results And Discussion

The thermoelectric properties of $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ are shown in Figures 3 through 7. The values are compared to those of

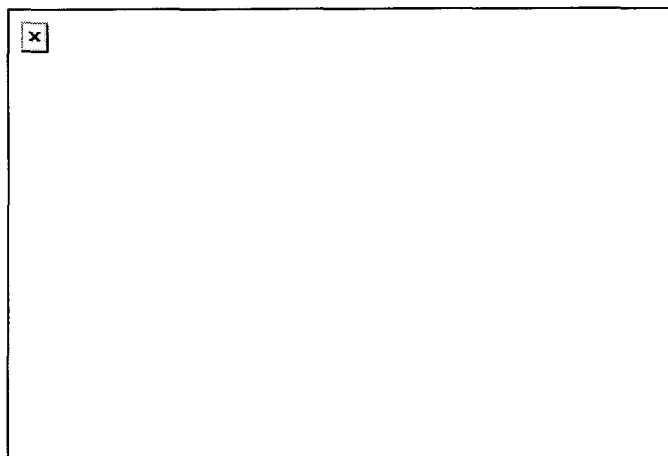


Figure 3. Resistivity measurements for $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ compared with CoP_3 .

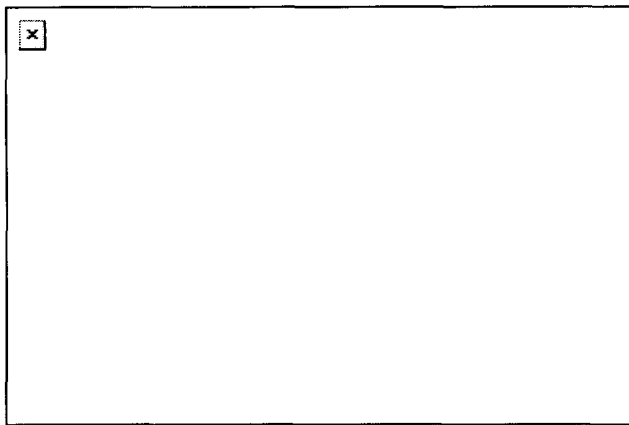


Figure 4. Mobility measurements for $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ compared with CoP_3 .

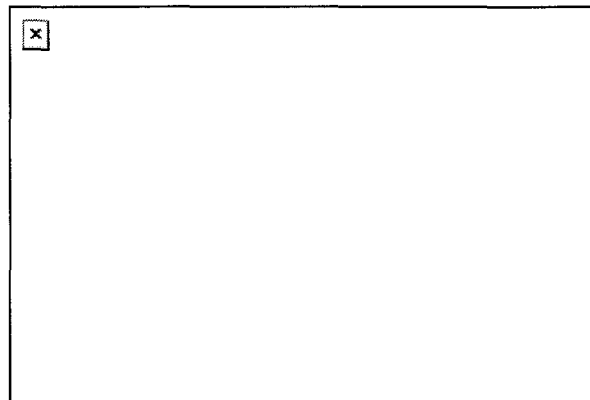


Figure 5. Carrier concentration measurements for $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ compared with CoP_3 .

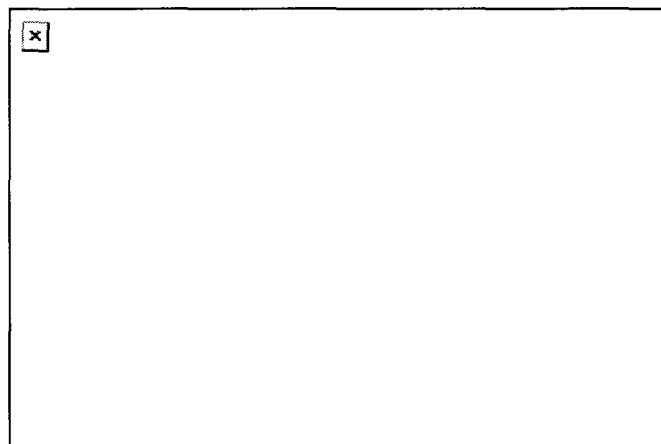


Figure 6. Seebeck measurements for $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ compared with CoP_3 .

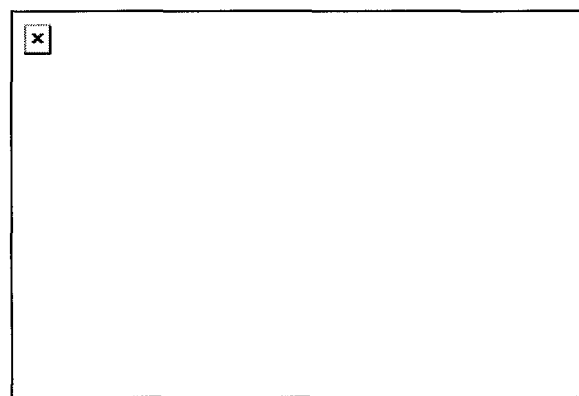


Figure 7. Thermal conductivity measurements for $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ compared with CoP_3 .

CoP_3 synthesized first at Stanford University and later at JPL. The Seebeck measurements appear to indicate that increasing the Ni concentration results in an increasing shift towards n-type behavior along with a reduction in thermal conductivity.

The electrical property measurements for the $\text{CoAs}_{(3-x)}\text{P}_x$

compounds are shown in Figures 8 through 11. No thermal conductivity measurements have been conducted as yet for

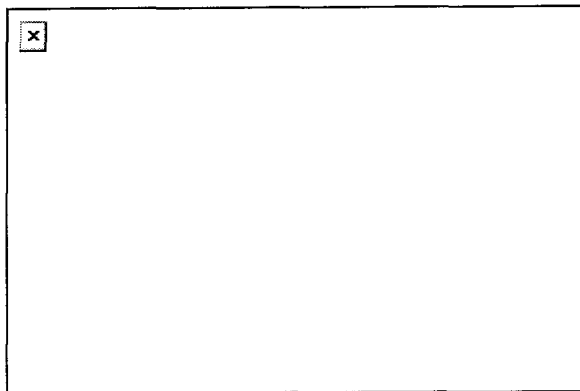


Figure 8. Resistivity measurements $\text{CoAs}_{(3-X)}\text{P}_X$ compared with CoP_3 and p-type CoAs_3 .

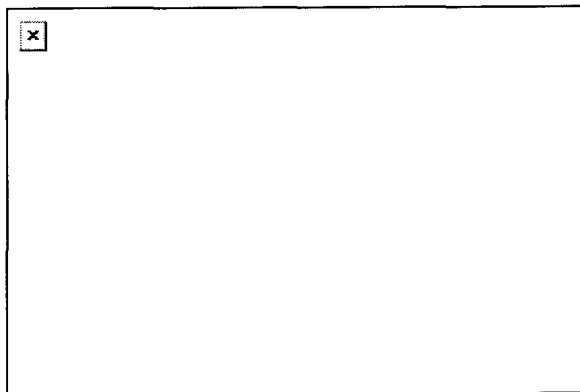


Figure 9. Mobility measurements $\text{CoAs}_{(3-X)}\text{P}_X$ compared with CoP_3 and p-type CoAs_3 .

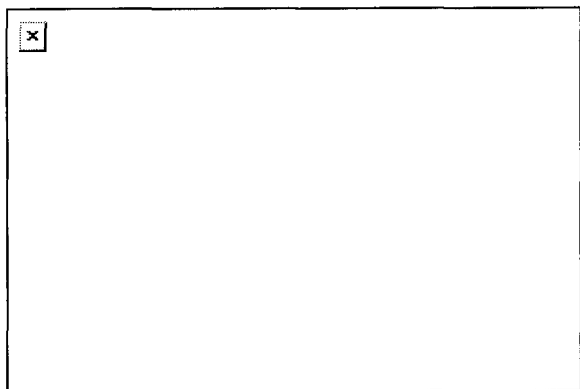


Figure 10. Carrier concentration measurements $\text{CoAs}_{(3-X)}\text{P}_X$ compared with CoP_3 and p-type CoAs_3 .

these samples. The values are compared with those for p-type CoAs_3 synthesized at JPL and two CoP_3 samples. The sample

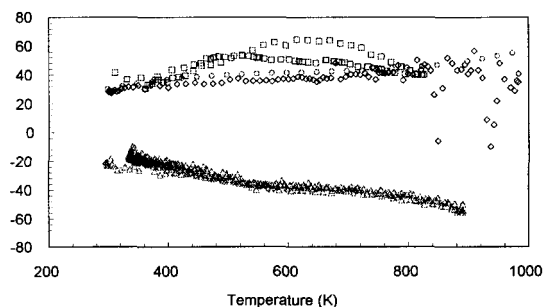


Figure 11. Seebeck measurements $\text{CoAs}_{(3-X)}\text{P}_X$ compared with CoP_3 and p-type CoAs_3 .

with the highest P concentration displays the highest mobility along with n-type characteristics.

Thermal Stability

Samples of CoP_3 have been undergoing continued annealing in static vacuum under both a temperature gradient and under isothermal conditions to determine the stability behavior []. The samples were placed in 35 cm long quartz ampoules instrumented with two thermocouples separated by 4 cm at the location of the sample as shown in Figure 12. For the gradient test the outer end of the ampoule extended

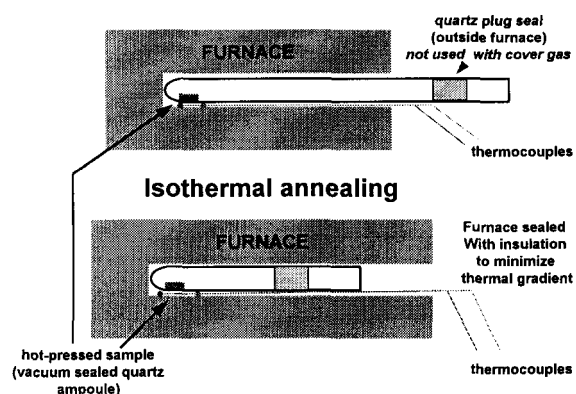


Figure 12. Isothermal and thermal gradient annealing test apparatus.

outside the furnace so as to allow any evolving species to condense away from the sample. The thermal gradient was about 39 K/cm across the sample. In the case of the isothermal test, the entire ampoule was inserted into a three-zone furnace that was adjusted to minimize any temperature gradient. The ampoule was instrumented with thermocouples in the same manner as the gradient test. The isothermal tests had thermal variations between about -0.17 K/cm and 0.25 K/cm across the samples. Figure 13 shows the mass loss rate for each of these tests. Comparative results are also shown from a CoSb_3 sample. The isothermal loss rate is observed to remain stable at temperature in excess of 1200 K indicating that no phase decomposition has occurred.

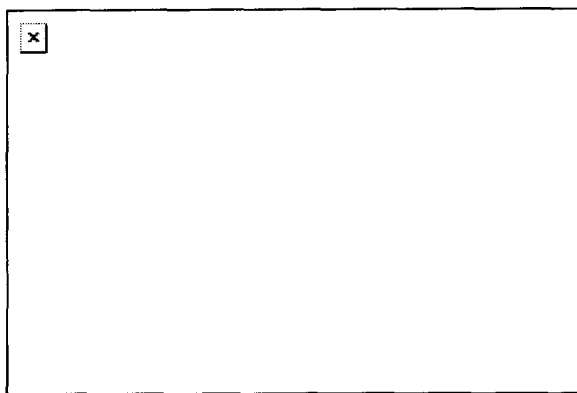


Figure 13. Isothermal and thermal gradient annealing results for CoP_3 in vacuum and in the presence of a 1 atm cover gas.

Additional thermal gradient tests were conducted to determine whether the loss rate could be reduced using a cover gas. In this arrangement the CoP_3 samples were exposed to a thermal gradient in the range already noted in a sealed ampoule back filled with 1 atm of argon (5% H). The results indicate about a 20 times reduction in loss rate using the cover gas.

Figure 14 shows the percentage weight loss from the samples in figure 13 as a function of annealing time. This graph more explicitly shows the relative loss compared with the total annealing time. The results at about 1100 K indicate a significant reduction in loss rate achieved in the presence of

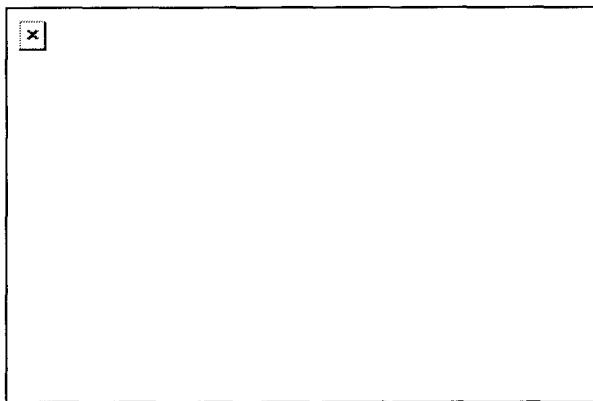


Figure 14. Weight loss percentage showing actual annealing times for CoP_3 samples in Figure 13.

a cover gas.

Conclusions

We have investigated the properties of solid solution of the type $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ and $\text{CoAs}_{(3-x)}\text{P}_x$ grown by direct synthesis from a stoichiometric pure elemental mixture. The first electrical and thermal measurements on bulk samples of these compound material have been presented. Results indicate that increasing the Ni concentration improves the

thermoelectric properties in $\text{Co}_{(1-x)}\text{Ni}_x\text{P}_3$ skutterudites. Although only a maximum of 7% Ni has been measured using electron microprobe analysis, unmeasured samples with expected Ni concentrations approaching 30% indicate the possibility of significant improvements in the Seebeck voltage along with a reduction in thermal conductivity. In addition, increasing the P concentration also appears to improve the thermoelectric properties in $\text{CoAs}_{(3-x)}\text{P}_x$ skutterudites. Samples with 10% P have displayed n-type Seebeck values along with a high mobility. Material stability at operational temperature is necessary for the success of these compounds. Thermal annealing results indicate that the loss rate can be reduced by more than an order of magnitude in the presence of a cover gas. This result indicates that a surface coating could be effective in increasing thermocouple longevity.

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